

ON SPECTRUM SERIES.<sup>1</sup>

## II.

IT is well that I should indicate the basis of these statements, and for this purpose I throw on the screen a very small part of the spectra of two or three different substances in order that you may see the way in which the work has been done. Take the lowest horizon. There we are dealing with zinc, and you see the way in which the triplets have been picked out. The triplet in each case, of course, supposing it is the remnant of a fluting, has its central line nearer to one side of the triplet than the other. All the triplets in the zinc spectrum are perfectly symmetrical from that point of view. If we take the upper spectrum—that of calcium—we find also that the triplets are formed in exactly the same way. We can quite understand the enormous labour which has been involved on the part of the inquirers I have named in working out from the spectra of a great many substances and from all the different regions of the spectrum, visible and photographic, these delicate triplets. In a

was far more simple than that of any other chemical elements. A short time ago, however, Prof. Pickering, in his magnificent work on the stars, to which I have already had the opportunity of referring, discovered a second series of lines. Not long after, Prof. Rydberg suggested that one of the most important lines seen in a large group of stars really represented a line of the principal series of hydrogen. That conclusion has been generally accepted, although the evidence is considered doubtful by some; so that we now assume that hydrogen has three series like helium and asterium, and we seem therefore to be on solid ground in one direction, at all events, in regard to some gases. We have another series of metals of low atomic weight, and which therefore chemically are supposed to represent a considerable simplicity; we find that in the case of lithium and sodium we also deal with three series, a principal series and two subordinate series. The series of lithium are just as beautiful in their rhythm as the other series to which I have referred. The same remark applies exactly to sodium. Now, it has recently been found that

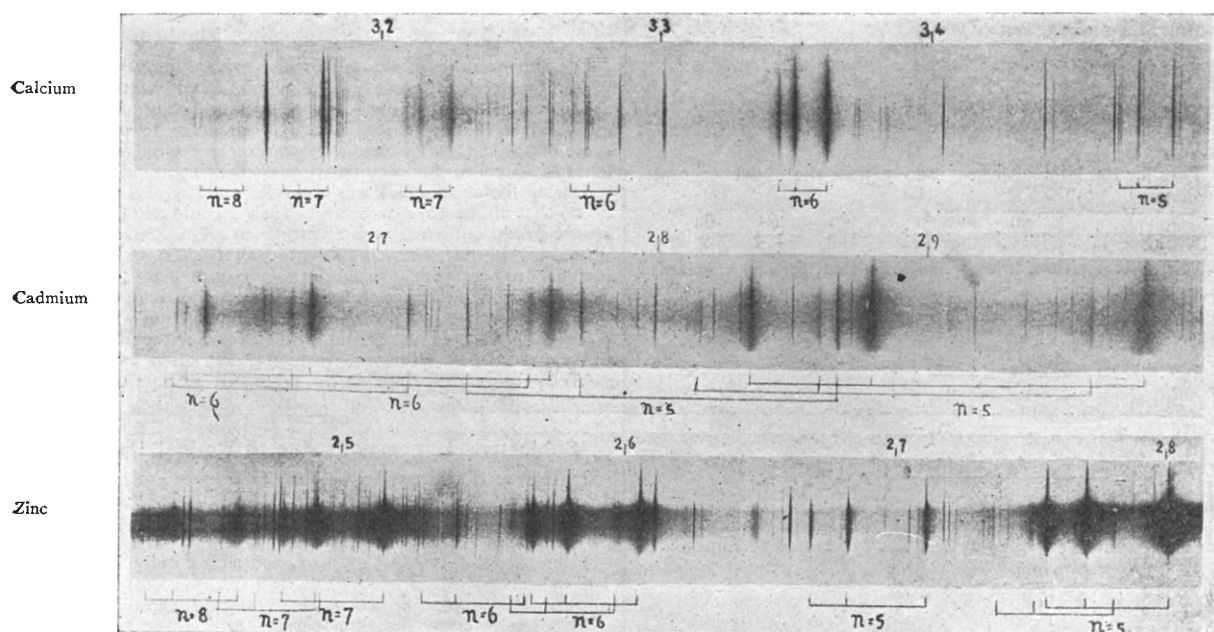


FIG. 6.—Parts of the spectra of calcium, cadmium and zinc showing the triplets.

great many cases they do not represent the strongest lines, those most easily seen, and they want a great deal of looking for.

I next pass on to some more general statements, which I am anxious to put before you for the reason that you will not find them stated in any literature that I am acquainted with; the subject has really not been generally discussed at all.

Some substances have three series, as in the case of helium and asterium. There are others like them; and the most remarkable case which I have to bring before you is that of hydrogen. We do not know the meaning of it yet, but it has to be taken into account in any consideration of these questions. Until a little time ago only one series was known in the spectrum of this gas, and it was thought that on that account the atom of hydrogen

sulphur and selenium also give us three series. We have a principal series and the first and second subordinates, but the suggestion of anything beyond these three is confined to one or two lines in each case. Next let us take another gas, and see what happens in the case of oxygen. *We have six series*, that is twice as many as we know of in hydrogen, helium, asterium, lithium, sodium, sulphur, and so on. I should say that so far as that goes we are in the same condition that we were some time ago when we imagined that the gas obtained from the mineral cleveite was really a single gas with six series. Very many arguments have been employed to show that that view is probably not an accurate one; so that some are prepared to separate the cleveite gases at spark temperatures into two, calling one helium and the other asterium. That brings these two constituents of the cleveite gas then to the same platform as hydrogen with the recent developments, lithium, sodium, sulphur, &c. If we come to consider this extraordinary condition in the case of

<sup>1</sup> A Lecture to Working Men, delivered at the Museum of Practical Geology, on May 1, by Prof. Sir Norman Lockyer, K.C.B., F.R.S. (Continued from p. 370.)

oxygen a little further, we find that the six series only after all pick up the oxygen lines seen at a low temperature, and that if we employ a high temperature to observe the oxygen spectrum, that is to say, if we use an induction coil, a jar and an air break, we find a very considerable number of lines indeed which have no connection whatever with the series. And we are face to face with this very awkward fact, that in the case of oxygen there are more lines which we cannot get into a series than there are lines in the six series which we have attributed to that chemical substance. Here, therefore, we begin certainly to get into difficulties. The inquiry is not so straightforward, the conditions are not so constant, as we might have expected them to be.

Here then we have instead of three series twice that number, and these only account for about half the lines. Now, let us look still a little further. The next point is that in the case of other substances *we have no principal series*, but only two subordinate ones. This happens in the case of magnesium, calcium and strontium. We have only two series in the case of magnesium, two in calcium, and two in strontium. In all those three

certain number of these lines has been picked up to form the series, but we get numerous lines which have been left over after all attempts to sort them into series have been made.

I have now to bring before you another consideration. We are dealing in the case of calcium and magnesium with arc temperatures, but I showed you in my first lecture that in the case of calcium and magnesium the all-important lines in the hottest stars were lines seen at the temperature of the spark. I have added these lines to the diagram, and you will see that there is not the slightest trace of those lines having been picked up in the series. So that the further we go, the more we seem to get away from that beautiful simplicity with which we began. I take you now to another group of substances, namely, tin, lead, arsenic, antimony, bismuth and gold, and I might mention more. No series whatever have as yet rewarded the many attempts of those who have tried to get those metals and non-metals on all-fours with those previously investigated. It remained for Kayser and Runge to point out that it looked very much as if this complete absence of series was connected with the melting point of the substances with which they had

been dealing. So long as the melting point was low, as in the case of sodium and lithium, the normal three series would show at low temperatures; and, further, there were no lines over. But, when you get to these substances with high melting points, there is no series at all, and of course it is suggested that therefore there must be intermediate stages; and that really seems to be a very valid suggestion indeed, and one which in all probability will enable us to get over some of the difficulties. They point out that in the case of lithium, sodium, potassium, &c., all the lines are picked up, and that in the case of copper, silver and gold the series pick up only a very small proportion. There seems, therefore, to be a progression of complexity with the increasing melting point with regard to all the metallic substances which have so far been examined; of course this consideration does not touch the question of oxygen. Oxygen is a gas, hydrogen is a gas in consequence, of course, of their very low melting points, and you know that quite recently it has been found possible to liquefy both of them. So that there must be something

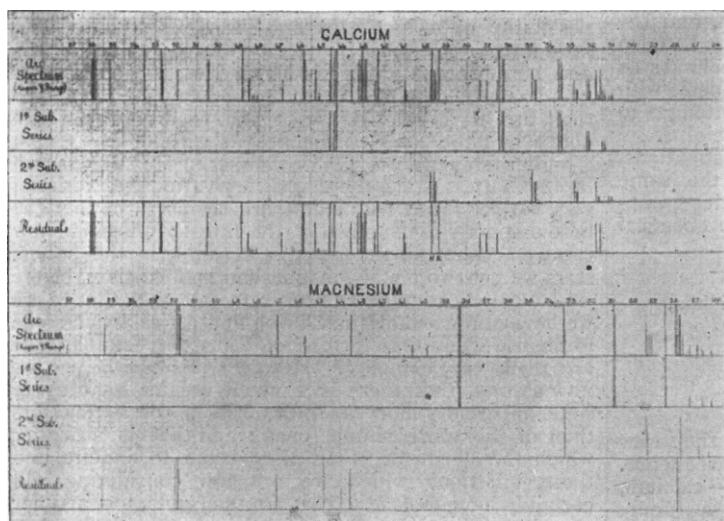


FIG. 7.—Map showing series and residual lines in spectra of calcium and magnesium.

we have a first and second subordinate series, but no principal series. I have studied the lines of calcium and magnesium, in the same way that the lines of oxygen were studied to see how many of the lines are picked up by the series. In the upper part of the diagram we have the lines seen in the arc spectrum of calcium, and in the two next horizons we have the lines picked up in the first and second subordinate series. The next horizon gives the residual lines—lines, that is, which have not been distributed into any of these series. You see that there is a large number outstanding just as in the case of oxygen, and it is very important indeed to note that the two lines H and K, which are more conspicuous in the spectrum of the sun than all the other lines of the spectrum, have not been caught by any of these researchers into the series of calcium. Therefore, with a reduced number of series, we seem to be getting still further from the simplicity we began with in the case of some of the permanent gases like hydrogen and helium. The same thing holds with regard to magnesium, the spectrum of which at the temperature of the arc has not so many lines in it as the spectrum of calcium. A

different in their case, and it seems extremely encouraging to find, therefore, that the same variation, the same breaking away from the law which I pointed out in the case of some of the metals, should really occur also in a gas, because it seems as if we shall be able to explain the phenomena in both cases by supposing that there is a condition of greater complexity, and that when we follow up this line of greater and greater complexity, whether in a gas such as oxygen, or in a solid such as gold, we do not get the simple series, because at the temperatures we employ we are still far from the simple condition which we can get at in some gases and in some metals with low melting points. The table gives the relation between the melting point and the percentage of lines sorted into series. Thus, in the case of barium with a high melting point we get no lines at all represented in the series; then we gradually get up to 100 per cent. in the case of lithium. But then again, as in the case of oxygen, when we come to mercury, which is also of low melting point, instead of getting 100 per cent. we only get about 25 per cent. of the lines represented in the series.



Relation of series to melting points.

Element	Melting point	Percentage of series lines
Barium ... ..	1600°	0
Gold ... ..	1200	4
Copper ... ..	1050	6
Silver ... ..	960	26
Strontium ... ..	700	20
Calcium ... ..	700	34
Magnesium ... ..	600	64
Zinc ... ..	410	80
Cadmium ... ..	320	50
Lithium ... ..	180	100
Sodium ... ..	90	100
Cæsium... ..	62	100
Potassium ... ..	58	100
Rubidium ... ..	38	100
Mercury... ..	-40	27

These matters, of course, have been very carefully inquired into, and among them I will just point out that Meyer has shown that if the wave-lengths of all the lines for  $n=\infty$  be calculated and put as ordinates, and the atomic weights as abscissæ, then all the points lie on a curve similar to that which gives the atomic volumes as functions of the atomic weights. He not only deals with the melting points, but he goes further and attempts to associate the melting points with the atomic weights.

The next consideration is that in these investigations, in some cases, the series have reproduced the same chemical group, but in some instances the series groupings, so to speak, are quite different from the chemical groupings.

The facts so far ascertained are as follows:—

- Group 1 ... Lithium, Sodium, Potassium, Rubidium, Cæsium.  
 „ 2 ... Copper, Silver, (Gold?).  
 „ 3 ... Magnesium, Calcium, Strontium.  
 „ 4 ... Zinc, Cadmium, Mercury.  
 „ 5 ... Aluminium, Indium, Thallium.

In the group of lithium, sodium, potassium, the series sequence follows absolutely the chemical sequence. But when we come to the chemical group—calcium, strontium, barium—you find it replaced by a group, magnesium, calcium, strontium, while barium is not used at all. That is a very remarkable departure, and it shows that we have to consider the various conditions which we observe in passing from group to group.

From *group to group* with increasing atomic weights the series back towards the violet. Thus, as the limit of a series is represented by the first constant for the first subordinate of the four groups, the limit lies

- Between 2858.6 and 1974.3 for Lithium, Sodium, Potassium, Rubidium, Cæsium.  
 „ 3159.1 „ 3078.2 „ Copper, Silver, Gold.  
 „ 3979.6 „ 3103.0 „ Magnesium, Calcium, Strontium.  
 „ 4294.5 „ 4015.9 „ Zinc, Cadmium, Mercury.

In *each group* with the increasing atomic weight the spectrum advances continually towards the red end; that is, in exactly the opposite direction we observed before.

Having dealt with these details, there are several other general questions which I should like to say a word about, because it is evident that we are here in presence of the beginning of a new attack on the nature of the chemical elements.

Let us attempt to compare these simplest results obtained by this newest form of spectrum analysis, in other words the simplest series, with the earliest stellar forms.

We found that the hottest stars contained hydrogen, helium, and asterium. Well, we have found that those substances have the simplest series; that is to say, one set of three. I told you that it was more than probable, although it is not absolutely established, that the lithium group of metals is also represented in stars of very high temperature. There, again, we have the simple series of one set of three. About sulphur we do not yet know positively, but it is probable, I think, that sulphur may exist in the hot stars. There, again, we get another simple set of three; so that for three perfectly certain members of the hottest stars, together with one in all probability and one doubtful, we are dealing with the simplest series in the hottest stars.

But now comes the remarkable fact that side by side with these simple substances we get in the hottest stars magnesium and calcium. We cannot suppose that the absence of the principal series there means a greater simplicity, because I have shown you that only about half the lines in the spectrum of each of these substances has yet been picked up in the series, and if the series represent the vibrations of a single particle, of course the lines which are not represented in the series, by theory must represent the vibrations of some other particles. So that there we are face to face with the possibility of a much greater complexity. Coming a little further down in stellar temperatures we find oxygen, and here we deal with six series instead of three, or two, as in the case of magnesium and calcium; and even then, as I have pointed out to you, we do not deal with above half the lines of the gas as we can see them at a higher temperature. This, then, seems to suggest that in the hottest stars there are very various stabilities of very various forms. In fact, there seems to be there as here distinctly the survival of the fittest; otherwise how can we account for the fact that certainly in the hottest stars we get two metals, magnesium and calcium, before we have indication of any other metals, and that where we have those metals and bring our series touch-stone to them we find that instead of being very simple they are really very complex? However this may be, we are now assured that there is a much greater quantity of some apparently more complex forms in the hotter stars than of the more simple ones; and that is a matter which the chemists, when they come to inquire into these questions which we are now considering, will certainly have to face. This fact suggests, too, another very interesting question which has some relation, perhaps, to some of those drawings that I have thrown on the screen from Lyell's Elements, which showed that a great many simple organic forms appear in the stratigraphic series at a late period; that some of the simplest forms died out, others remained. Now, it may be that some of the more simple forms in inorganic evolution, as in organic evolution, really represent later introductions; but, however this may be, it is perfectly certain that we have not an absolute parallel between the results of the spectroscopic observations of series and the spectroscopic observations of stars. The accompanying table will show very generally how the matter stands. The chief points to refer to are the gaps in the table showing the principal series and the first and second subordinate series. We have the metals arranged in the order of Mendelejeff's groups. You will observe that after the first metals we practically deal with no principal series at all until we come down at the bottom to oxygen, sulphur and selenium. The same thing happens with the subordinate series so far as the existence of single lines and double lines are concerned. Now, it is a curious point that in the case of several of those substances in which no principal series has been detected, certain lines in the ultra-violet of considerable strength have been observed which may ultimately turn out to represent principal series. Of course, if that should be so it will make the inquiry a

very much simpler one than it appears to be at present, and it may possibly break down that terrible amount of uncertainty and irregularity which it has been my duty to point out to you in the series so far examined.

there is no fluting from one end of the spectrum to the other.

Rydberg has suggested that an investigation of the so-called "longest-lines" of the various substances may

	Mendff. groups.	Atomic weights.	No. of series.	No. of principal series.	Principal series.			1st and 2nd subordinate.			REMARKS.	Per cent. of total number of lines picked up by K. and R.	Per cent. of lines of intensity 10, picked up in series.	Melting points, degrees C.
					Single.	Double.	Triplets.	Single.	Double.	Triplet.				
HYDROGEN	—	1	3	1	—	Double ?	—	—	Double	—	—	100	100	—
HELIUM ...	—	—	3	1	Single	—	—	—	Double	—	{ In sub. series the double represents strong member with faint companion. Helium really gives a spectrum of six series, but one set of three series has been called Asterium.	100	100	—
ASTERIUM	—	—	3	1	Single	—	—	Single	—	—		100	100	—
LITHIUM	I.	7.0	3	1	—	Double ?	—	—	Double ?	—	{ The pairs in all cases widen as the atomic weights increase.	100	100	180
SODIUM ...		23.0	3	1	—	Double	—	—	Double	—		100	100	90
POTASSIUM		39.0	3	1	—	Double	—	—	Double	—		100	100	58
RUBIDIUM		85.2	1	1	—	Double	—	Not observed		—		100	100	38
CÆSIUM ...		133	1	1	—	Double	—			—		100	100	62
COPPER ...	I.	63.4	2	0	—	—	—	—	Double	—	{ Each element contains in the ultra-violet a very strong pair of lines which may be principal series.	6	—	1080.5
SILVER ...		107.6	2	0	—	—	—	—	Double	—		26	—	960
GOLD ...		196.7	0	0	—	—	—	—	—	—		?	—	1061.7
MAGNESIUM	II.	24.3	2	0	—	—	—	—	—	Triplets	{ 2852.2 and some pairs not picked up by these series. Some more triplets and pairs not picked up by these series.	64	55	600
CALCIUM		39.9	2	0	—	—	—	—	—	Triplets		34	17	700
STRONTIUM		87.4	2	0	—	—	—	—	—	Triplets		20	7	700
BARIUM ...		136.8	0	0	—	—	—	—	—	Triplets		—	—	475
ZINC ...		65.1	2	0	—	—	—	—	—	Triplets		80	43	410
CADMIUM	II.	111.7	2	0	—	—	—	—	—	Triplets	{ In each case a very strong broad reversed line in the ultra-violet may be principal series.	50	14	320
MERCURY		199.8	2	0	—	—	—	—	—	Triplets		27	12.5	-40
ALUMINIUM	III.	27.0	2	0	—	—	—	—	Double	—	{ No series have been discovered, but there seem to be groupings of lines which recur very frequently. The lines do not form series.	—	25	654.5
INDIUM ...		113.7	2	0	—	—	—	—	Double	—		—	25	176
THALLIUM		203.7	2	0	—	—	—	—	Double	—		—	17	282
TIN ...	IV.	117.8	0	0	—	—	—	—	—	—	{ These probably have six series. One strong triplet is observed which may be principal series of second set of three series.	—	—	232
LEAD ...		206.4	0	0	—	—	—	—	—	—		—	—	326
ARSENIC	V.	74.9	0	0	—	—	—	—	—	—	{ No series have been discovered, but there seem to be groupings of lines which recur very frequently. The lines do not form series.	—	—	450
ANTIMONY		119.6	0	0	—	—	—	—	—	—		—	—	629.5
BISMUTH		207.5	0	0	—	—	—	—	—	—		—	—	270
OXYGEN ...	VI.	15.88	6	(2)	—	—	Triplets	—	—	Triplets	{ These probably have six series. One strong triplet is observed which may be principal series of second set of three series.	—	—	—
SULPHUR		31.8	3	1	—	—	Triplets	—	—	Triplets		—	—	114
SELENIUM		78.5	3	1	—	—	Triplets	—	—	Triplets		—	—	217

Another matter of considerable importance to us in attempting to arrange the chemical elements along this line of series—and it is work that is sure to be done now that the matter is once started—is to endeavour to see if there is any strict relation between those chemical substances which give us these simple series and those which are more apt to provide us with those exquisite rhythmic flutings. In some of the elements the flutings and the proportions of them from one end of the spectrum to the other are very remarkable, but in other metals the wonderful thing about them is that practically

eventually help us in our inquiries. I will tell you what the longest-line means. If we examine a light source by pointing the spectroscope directly at it, of course the rays from every part of the light source enter the instrument; but if we throw an image of the light source on the slit of the spectroscope, then those particles which exist furthest from the centre will be visible furthest from the image of the centre, and therefore if they are visible enough to give spectra, we should get long lines stretching from the centre to the very limit at which their light is visible enough to be utilised by the instrument. As a

matter of fact we do see some very long lines in this way in the case of some substances, and these of course appear to be quite distinct from the shorter lines which are limited to the exact centre of the spark or the arc; to the region, that is, in which the very highest temperature is at work. Rydberg has shown that in a considerable number of cases long lines seem to have a very considerable importance, and on that account it is well worth inquiring into. Rydberg's investigations of the members of the first three groups of the periodic system led him to conclude that the long lines form pairs or triplets, which in the case of each element are characterised by a constant difference ( $\nu$ ) in the number of waves of the components. For each group of elements shown in Mendeléeff's table, this value he finds increases in a ratio somewhat exceeding the *square* of the atomic weight.

What, then, is the general result of our inquiry, taking series in inorganic evolution to represent the cells which are microscopically studied in the case of organic evolution? I think you will agree that the evidence is that, however simple the organic cell may be, the chemical units in the case of any substance represented to us by the movements which are written out by these series must possess different degrees of complexity. I have already told you that a little time ago it was imagined that hydrogen was rendered visible to us by such simple vibrations that only one series of lines could be produced. If that is so, then it looks very much as if whenever we see three series of lines that three molecules or atoms, three different things, are in all probability at work in producing them. When we get six series, that points to a still greater complexity, and when as in the case of oxygen we get six series not accounting for half the lines, then we should be quite justified, I think, in supposing that oxygen was one of the most complex things that we were brought face to face with in our studies of series. When we come to metals where there are no series at all, what do we find? We find that we are dealing with substances with high melting points—that is to say, we cannot bring them down easily to those mobile states represented by the free paths of a permanent gas; and it is quite easy to suppose, on that account alone, that we do not see the vibrations of any of the more simple forms. Therefore, I think it is perfectly certain that we have not universally got down to the equivalent of the cell-level in our study of chemical forms.

With regard to this question of the relation of the two evolutions inorganic and organic, I have still one more diagram which will give an idea of the place of organic evolution in regard to inorganic evolution in the scale of time. I do not want you to pay too much attention to this diagram, because it is entirely hypothetical; but it is constructed on the simplest principles, so that it shall go as little wrong as may be. I begin by drawing a line at the bottom, which represents the zero of temperature; certain temperature values are indicated on the left-hand side of the diagram. Then we have the assumption that a star loses an equal amount of heat in an equal period of time. In that way, then, you see at the bottom we have relative times, as at the side we have temperatures, in Centigrade degrees. Water freezes at a certain temperature above absolute zero, and boils at a certain other point; these are marked on our temperature scale. Then we have to remember that about half-way between the boiling point and the freezing point, all the organic life with which we are familiar on this planet, from the geological evidence and our own experience, must have gone on at a temperature of somewhere about, let us say, from 50° to 40° Centigrade. There, then, we get the limit of organic life in relation to the possible inorganic life, represented by the various chemical changes in the stars. We know from laboratory statements that

the stars of lowest temperature are about the same temperature as that of the electric arc, which is about 3500° C., and so we put the Piscian stars there. It has also been stated by Mr. Wilson lately that the temperature of the sun measured by several physical methods is something between 8000° and 9000° C., so that we put there the Arcturian stars. Of course we have no means of determining the temperatures of the hotter stars, so I have ventured to make a very modest supposition that possibly we get about half the difference of temperature between those stars as we have found between the Piscian and the Arcturian stars from experiments on the earth. That will give us roughly something like 5000° C. We find then that if we assume equal increments of temperature for each of the different genera of stars that I brought before you in the second lecture, we get a temperature at the top of the diagram of something like 28,000° Centigrade. All we have to do, then, is, to draw a diagonal line on which to mark the various temperatures considered. On this the organic evolution, which represents everything which has taken place with regard to living forms on the surface of our planet from the pre-Laurentian times to our own, is represented by a small dot. It looks, therefore, very much as if these recent results of spectrum analysis, which it has been my duty and my pleasure to bring before you in this course of lectures, may probably be of some value in the future, because they deal with a multitude of changes and a period of time compared with which all the changes discussed by the geologists are almost invisible on a diagram of this size. Not only shall we have probably some help in determining this scale, but I think that, as I have already indicated to you, the wonderful similarity between the substances contained in the organic cell and those which would most likely be free when the greatest amount of chemical combination had taken place on the surface of the cooling world, will throw some light on the basis of organic evolution itself.

In that way, then, we have really been only continuing courses of lectures given here formerly, which had to do with Man's Place in Nature, and with the Sun's Place in Nature; and I think you will agree that we have found fresh grounds for thinking that the more different branches of science are studied and allowed to react on each other, the more the oneness of Nature impresses itself upon the mind.

#### NOTE ON THE DISCOVERY OF MIOLOANIA AND OF GLOSSOTHERIUM (NEOMYLODON) IN PATAGONIA.<sup>1</sup>

SINCE 1877, when I discovered the Tertiary Mammalian beds of Santa Cruz, in Patagonia, I have been looking for proofs of the ancient connection between the new uplifted lands of the southern part of the American continent and the other lands of the Southern Hemisphere—Africa and Australia. During my subsequent travels in the interior of the Argentine Republic, including Patagonia, my interest in that connection has been increasing, and I have discovered additional evidence, which showed me the former greater extension to the east, in comparatively modern times, of the actual existing lands. The splendid results of the researches made by the La Plata Museum in Patagonia have revealed a greater number of lower forms of vertebrates, including numerous marsupialia, some of which seem to me closely related to the mammals of the Pleistocene fauna of Australia, and among them *Pyrotherium* and *Diprotodon*. I think that my suggestion has an indubitable

<sup>1</sup> By Dr. Francesco P. Moreno, Director of the La Plata Museum.

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